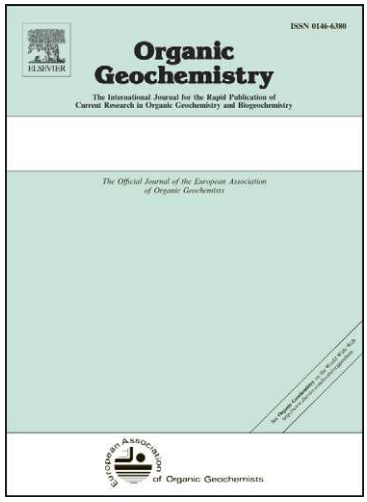
Towards reconstruction of past fire regimes from geochemical analysis of charcoal

Wolf, Mareike ; Lehndorff, Eva ; Wiesenberg, Guido L B ; Stockhausen, Martin ; Schwark, Lorenz ; Amelung, Wulf

Abstract: Production of charcoal has accompanied human life from the beginning. We aimed at evaluating the degree to which the chemical signatures of charcoal may serve as a fingerprint for burning conditions. After a compilation of fire literature we differentiated three typical fire regimes [grass and forest ground (285 ± 143 °C), shrub (503 ± 211 °C) and domestic fires (797 ± 165 °C)] and three main factors impacting on charcoal formation: charring duration, temperature and fuel. For fingerprint calibration and validation, typical fuels of prehistoric burning events (wood and grass) were charred under laboratory conditions (300-700 °C; varying duration) and compared with residues from natural fires in SE Europe. Analysis comprised assessment of benzene polycarboxylic acids (BPCAs), organic carbon (Corg) content, nitrogen content, oxygen index (OI: CO2/Corg) and hydrogen index (HI: HC/Corg), temperature of maximum heating (Tmax) and mid-infrared spectroscopy (MIRS). All parameters including mass loss increased with increasing combustion temperature, but were unaffected by charring duration. Grass charcoal had consistently lower Corg content and HI than wood, but values showed a bias towards the natural charcoals, probably because the latter contained higher amounts of mineral matter or were combusted under greater O2 supply. Nevertheless, natural charcoals could be differentiated into forest ground fires (B5CA/B6CA 1.3-1.9; OI >20; intense CH2 stretching, Tmax <488 °C) and grass fires (B5CA/B6CA 0.8-1.4; OI >20; weak CH2 stretching, Tmax <425 °C), whereas domestic fires revealed B5CA/B6CA values <0.8, OI values <20 and little MIRS absorbance. In summary, it appears possible to reconstruct fire regimes from the temperature sensitivity of BPCA patterns, Tmax, OI and aromatic and aliphatic MIRS signals, whereas assignment of fuel source was less reliable.

DOI: https://doi.org/10.1016/j.orggeochem.2012.11.002



Towards reconstruction of past fire regimes from geochemical analysis of charcoal

Mareike Wolf, Eva Lehndorff, Guido L.B. Wiesenberg, Martin Stockhausen, Lorenz Schwark, Wulf Amelung

PII: S0146-6380(12)00226-4
DOI: http://dx.doi.org/10.1016/j.orggeochem.2012.11.002
Reference: OG 2877

To appear in: *Organic Geochemistry*

Received Date: 5 July 2012
Revised Date: 26 October 2012
Accepted Date: 1 November 2012

Please cite this article as: Wolf, M., Lehndorff, E., Wiesenberg, G.L.B., Stockhausen, M., Schwark, L., Amelung, W., Towards reconstruction of past fire regimes from geochemical analysis of charcoal, *Organic Geochemistry* (2012), doi: http://dx.doi.org/10.1016/j.orggeochem.2012.11.002

Towards reconstruction of past fire regimes from geochemical analysis of charcoal

MareikeWolf [a,*], Eva Lehndorff [a], Guido L.B. Wiesenberg [b,c], Martin Stockhausen [d], Lorenz Schwark [d], Wulf Amelung [a]

[a] *Institute of Crop Science and Resource Conservation – Soil Science and Soil Ecology, University of Bonn, Nussallee 13, 53115 Bonn, Germany*

[b] *Department of Agroecosystem Research, University of Bayreuth, 95440 Bayreuth, Germany*

[c] *Department of Geography, University of Zurich, 8057 Zurich, Switzerland*

[d] *Institute for Geoscience, University of Kiel, 24118 Kiel, Germany*

*Corresponding author: Tel.: +49 228 739369; fax: +49 228 732782.

E-mail address: mareike.wolf@uni-bonn.de (M. Wolf).

ABSTRACT

Production of charcoal has accompanied human life from the beginning. We aimed at evaluating the degree to which the chemical signatures of charcoal may serve as a fingerprint for burning conditions. After a compilation of fire literature we differentiated three typical fire regimes [grass and forest ground (285 ± 143 °C), shrub (503 ± 211 °C) and domestic fires (797 ± 165 °C)] and three main factors impacting on charcoal formation: charring duration, temperature and fuel. For fingerprint calibration and validation, typical fuels of prehistoric burning events (wood and grass) were charred under laboratory conditions (300-700 °C; varying duration) and compared with residues from natural fires in SE Europe. Analysis comprised assessment of benzene polycarboxylic acids (BPCAs), organic carbon (C_{org}) content, nitrogen content, oxygen index (OI: CO_2/C_{org}) and hydrogen index (HI: HC/C_{org}), temperature of maximum heating (T_{max}) and mid-infrared spectroscopy (MIRS). All parameters including mass loss increased with increasing combustion temperature, but were unaffected by charring duration. Grass charcoal had consistently lower C_{org} content and HI than wood, but values showed a bias towards the natural charcoals, probably because the latter contained higher amounts of mineral matter or were combusted under greater O_2 supply. Nevertheless, natural charcoals could be differentiated into forest ground fires (B5CA/B6CA 1.3-1.9; OI >20; intense CH_2 stretching, T_{max} <488 °C) and grass fires (B5CA/B6CA 0.8-1.4; OI >20; weak CH_2 stretching, T_{max} <425 °C), whereas domestic fires revealed

B5CA/B6CA values <0.8, OI values <20 and little MIRS absorbance. In summary, it appears possible to reconstruct fire regimes from the temperature sensitivity of BPCA patterns, T_{max}, OI and aromatic and aliphatic MIRS signals, whereas assignment of fuel source was less reliable.

Keywords: black carbon, soot, charred grass, fire temperatures, prehistoric fires

1. Introduction

Incomplete combustion of biomass-derived fuels produces a continuum of structurally preserved organic matter (OM), differentlyaromatic structures re-condensed to differing extents and ash. The aromatic structures are particularly recalcitrant (black carbon, BC; Brodowski et al., 2005a; 2006) and so may reside in soil and sediments for up to several millennia or even longer (e.g. Masiello and Druffel, 1998; Scott 2000; Antal and Grønli, 2003; Grasby et al., 2011). The combustion residues may therefore preserve information about past burning and related environmental conditions (Knicker, 2011) or human-environment interaction. However, it is difficult to utilise this information because of a lack of analytical methods that allow complete characterisation of the BC continuum in environmental matrices (Hammes et al., 2007; Roth et al., 2012).

With abundant O_2 supply, OM may be burned completely, with only ash remaining (Misra et al., 1993); however, if the process is interrupted or O_2 supply is limited, charcoal rather than ash remains (Beaumont, 1985; Braadbaart and Poole; 2008). The organic combustion residue is often differentiated into charcoal and soot BC. Charcoal BC is commonly defined as a solid, often woody, relict of incomplete combustion (Goldberg, 1985; Novakov, 1984; Preston and Schmidt, 2006; Keiluweit et al., 2010), while higher burning temperatures produce new condensed forms of polyaromatic carbon from the gas phase (soot BC; Novakov, 1984; Preston and Schmidt, 2006; Apaydin-Varol et al., 2007). In general, a lower charring temperature

of ca. 400 °C preferentially leaves charcoal behind, while a charring temperature of 600 °C and higher promotes the formation of soot (Apaydin-Varol et al., 2007; Keiluweit et al., 2010). Keiluweit et al. (2010) used near-infrared spectroscopy to illustrate how - upon combustion - the proportion of initial woody structures is lost, accompanied by a loss of H_2O and CO_2, finally becoming reorganized into polyaromatic structures. McBeath et al. (2011) could show that, on top of re-condensation and aromatization, soot particles increasingly coagulate on the charcoal with increasing combustion temperature. The overall properties of the BC particles therefrom change; however, these variable properties also offer a chance to relate the BC properties to its conditions of formation.

Multiple factors characterize the "thermal profile" of different fire regimes (Livingstone Smith, 2001). Several studies of fire temperature revealed that it varied from ca. 80 °C in grass (grass biomass) to 950 °C in domestic fires (woody fuel; Table 1-SI in Supplementary Material; Stinson and Wright, 1969; Bailey and Anderson, 1980; Cohen-Ofri et al.; 2006; Sah et al., 2006; Dupuy et al., 2007; Fierro et al., 2007). We consider this large variation as the greatest challenge for the reconstruction of past fire regimes. Other factors that likely have an impact on charcoal production are fuel type, resin content (especially in softwood), wind speed (affecting O_2 supply), moisture (Archibold et al., 1998) and duration of charring (Braadbaart and Poole, 2008). Some of these factors, such as moisture, wind speed and fire temperature, correlate (Stinson and Wright, 1969); others, such as fuel type

have to be tested in addition for their effect on geochemical fire reconstruction proxies.

Different fuel sources, such as grass and wood, differ in the proportions of lignin and cellulose and, hence, in their physical structure (Czimczik et al., 2002; Braadbaart and Poole, 2008; Knicker, 2011). Accordingly, a higher amount of organic carbon (C_{org}) remains in charred wood than in charred grass (Hammes et al., 2006). Besides, the fuel and therefore the resulting charcoal vary in the proportions of H, O, C and N (Haumaier and Zech, 1995; Hammes et al., 2006). The depletion in O and H from organic bonds reveals an insight into charcoal formation. Several authors have consistently reported, by way of elemental C, H and O analysis, ongoing "carbonization" (Haumaier and Zech, 1995; Baldock and Smernik, 2002; Hammes et al., 2006; Keiluweit et al., 2010; Schneider et al., 2010). The rapid loss of H and O is related to dehydration, decarboxylation, demethylation and aromatization (Baldock and Smernik, 2002; Almendros et al., 2003; Keiluweit et al., 2010). Hence, the degree of carbonization of charcoal and therefore the combustion temperature can be estimated approximately using the hydrogen index (HI) and oxygen index (OI; Almendros et al., 2003). Yet, we are not aware of a study which has tried to relate a combination of these properties to both fuel type and combustion conditions.

A more detailed insight into the origin of charcoal might be achieved by characterizing in addition its quality (Keiluweit et al., 2010). Among the

different procedures available, the assessment of BC quality and amount from oxidation to benzene carboxylic acids (BPCAs) and mid-infrared spectroscopy (MIRS) were found to be most suitable (Bornemann et al., 2008; Keiluweit et al., 2010; Ziolkowski et al., 2011; Roth et al., 2012). Hence, we assumed that combining all approaches might provide a clue to both reconstructing the charring conditions and fuel source of the charcoal from geochemical fingerprint analysis.

The main goal was to elucidate whether or not, and to which degree, typical charring conditions for vegetation fires may be reconstructed on the basis of MIRS, BPCA analysis, elemental analysis (C, N) and Rock Eval parameters (OI, HI, T_{max}) for different charcoal samples. The main factors for consideration were charring temperature, charring duration and change in fuel type (hardwood, softwood and grass).

2. Material and methods

To attempt to assign the properties of BC to different fire events, we first performed a literature survey for analysis of common fire temperatures and associated properties (e.g. fuel type, wind speed; see Table 1-SI for details).

2.1. Wood and grass samples in combustion experiments

To test the feasibility of reconstructing past fire events in the Holocene, we used typical fuels used by prehistoric settlers in Europe. These were beech, apple and whitethorn as primary fuel in domestic fireplaces, as identified from pollen analysis, and einkorn and emmer grass burned in prehistoric agricultural plots (Knörzer et al., 1999). In addition, pine wood was processed as a typical fuel from Mediterranean temperate forests. Hence, samples comprised both soft- and hardwood. Apple and whitethorn wood were collected at the beginning of the growing season (March 2010; Garden of the Horticulture Department and field station at 54550 Rengen, University of Bonn, Germany). Einkorn and Emmer grass were provided by A. Börner [Leibniz Institute of Plant Genetics and Crop Plant Research (IPK), Gatersleben, Germany] and were collected in the growing season after threshing (August 2010). Grass samples were dried at 40 °C, cut to ca. 20 cm length and bundled to a diameter of < 7 cm. All wood samples were dried at 40 °C and frozen with liquid N_2 for crushing to ca. 5-10 cm length and < 1 cm diameter. They were then combusted as outlined below.

146 *2.2. Production of BC calibration material in combustion experiments*

147 To relate geochemical proxies to fire regime, we produced BC calibration
148 material by combusting the above fuels in the laboratory. Three set ups
149 were chosen (Table 1) to reveal combustion residue characteristics. Based on
150 fire regimes as assigned from the literature survey (Table1-SI, Table 2), set
151 ups (Table 1) were typical for A, domestic fires (i.e. high temperature and
152 high heating rate) and B, slash and burn fires (i.e. low temperature and
153 slow heating rate). Different degrees of combustion duration were chosen to
154 cover a reasonable duration for fires in archaeological situations (Table 1).
155 In experiment C, charcoal samples were produced in a thermo-sequence to
156 systematize the change in wood transformation and charcoal formation. All
157 experiments were carried out using a split tube furnace with external
158 control (Carbolite, Ubstadt-Weiher, Germany), equipped with synthetic air
159 (AIR LIQUIDE, Düsseldorf, Germany; 50 l synthetic air, 5.0 hydrocarbon
160 free, purity 99.999 %; 20.5% O_2 in N_2) supply to ensure a constant gas flow
161 (60 ml min^{-1}), providing one way transport of condensate. Exact temperature
162 was assured by heating with three internal thermocouples and controlled
163 via one external thermocouple situated in the middle of the combustion
164 tube. Charcoal residues were collected after passive cooling to ca. 50 °C.

165 *2.3. Natural charcoal samples*

166 To test the validity of the fingerprints for fire regime reconstruction, we
167 looked for natural charcoal samples from real wild and anthropogenic fires.

We used samples collected after forest ground fires in oak stands in Russia and one oak slash pile (n=4). These samples were obtained in the region of Voronezh on Chernozems one year after the fire event. In addition, charcoal samples from natural grass fires (n=8) were collected in Serbia on Haplic Chernozems of the Titel Loess Plateau near the village of Mosorin, ca. 25 km E of Novi Sad. There, charcoal samples were collected from the litter layer between a few days and weeks after the fire.

Domestic style fires were taken from a campfire (n=2) and additionally reproduced in a barbecue with (i) pure apple wood and a mixture of beech, birch and oak wood (30 to 60 min) and (ii) with beech and meat (chicken; 2 h). For the campfire, a constant O_2 supply assured a high combustion temperature. The burning experiments were carried out outdoors in November 2011 on dry days with a temperature of ca. 10 °C and wind speed 21 km h^{-1}. Samples were dried in an oven at 40 °C, homogenized with a mortar and pestle and milled in a ball mill (MM400, RETSCH, Haan, Germany). The domestic (barbecue) fire samples were additionally differentiated manually into solid charcoal residues > 2 cm ($char_{10cm}$) and solid charcoal residues < 2cm ($char_{2cm}$). The latter were lighter in colour, likely reflecting higher ash content (Table 2b-SI); however, since all other properties of these two size classes were identical, the different sizes of the domestic charcoals are not discussed further.

2.4. Chemical analysis

2.4.1. C and N

191 C_{org} content and N content were determined with a Fisons NA 2000
192 elemental analyzer. The method involves dry combustion to CO_2 and its
193 quantification using a heat conduction detector. To guarantee the complete
194 transformation of BC to CO_2, tungsten oxide (ca. 20 mg) was added as
195 catalyst to 3 mg charcoal. To remove inorganic C from the ash residue in the
196 combustion product, we added 5 ml 2 M HCl. Samples were added to a glass
197 fibre filter (GF 6), and vessel and filter were rinsed with deionized water
198 until neutral. Filters were dried in an oven for 2 h at 30 – 40 °C before C_{org}
199 and N analysis.

200 *2.4.2. Rock Eval parameters*

201 Rock Eval pyrolysis after Espitalié et al. (1977, 1985) and Bordenave et al.
202 (1993) was designed to discriminate labile hydrocarbons from thermally
203 altered, stable hydrocarbons and to quantify CO_2 emanating from O-
204 containing compounds via stepwise pyrolysis. Thereby the temperature
205 required for releasing and cracking of "altered hydrocarbons" is recorded
206 (T_{max}). Trapping of CO_2 up to 390 °C and subsequent release allows
207 quantification of O from OM. Compared with elemental analysis of C, H and
208 O, this method avoids overestimation of inorganically bound O and H, and is
209 thus free from contamination by, e.g., ash. The proportion of O and H in OM
210 is indicative for diagenetic (van Krevelen, 1950) or thermal degradation
211 (Haumaier and Zech, 1995). The measurements were performed with a Rock
212 Eval II instrument (VINCI, Nanterre, France). In brief, milled samples were
213 heated rapidly to a maximum temperature of 300 °C in an inert atmosphere,

214 thereby recording the amount of free hydrocarbons (S_1 signal; HC mg g^{-1}).
215 The temperature was then increased again to 550 °C at 25 °C min^{-1} in order
216 to assess the amount of hydrocarbons generated via thermal cracking of
217 stable OM (S_2 signal; flame ionization detector; HC mg g^{-1}). The maximum
218 generation of stable hydrocarbons during the S_2 peak temperature program
219 is recorded as T_{max} (i.e. $T_{max} \leq 550$ °C with the setup used here; if in reality
220 T_{max} was higher it could only be set to > 550 °C using the Rock Eval
221 equipment available to us). To measure the proportion of O-containing
222 compounds, a thermal conductivity detector recorded the released CO_2 up to
223 390 °C (S_3 signal: CO_2 mg g^{-1}). The S_2 and S_3 signals for the organic
224 compounds containing hydrocarbon and oxygen were then normalized to
225 C_{org}, thus giving the so-called HI or OI values, respectively (Espitalié et al.,
226 1977; 1985; Bordenave et al., 1993).

227 *2.4.3. BPCAs*

228 The BPCA method allows qualifying and quantifying BC in environmental
229 samples (e.g. Glaser et al., 1998; Hammes et al., 2008; Roth et al., 2012).
230 The method relies on the oxidation of condensed aromatic moieties in
231 charcoal to BPCAs by hot HNO_3 Glaser et al., 1998). The sum of carboxylic
232 acids after oxidation represents a marker for the total amount of
233 polyaromatic carbon (Glaser et al., 1998). The ratio of products with 5 to
234 products with 6 carboxyl groupss (B5CA/B6CA) serves as a measure for the
235 original degree of aromatic condensation in the charcoal. We followed the
236 revised protocol of Brodowski et al. (2005b). For BPCA assessment, 10 mg of

dried and milled charcoal was treated with 10 ml 4 M CF_3CO_2H (99 %, Sigma Aldrich, Taufkirchen, Germany) to remove polyvalent cations. The charcoal was then converted to BPCAs by oxidation with HNO_3 (8 h, 170 °C). After cleanup via a cation exchange column (Dowex 50 W X 8, 200–400 mesh, Fluka, Steinheim, Germany), the BPCAs were silylated and measured using gas chromatography with flame ionization detection (GC-FID; Agilent 6890 gas chromatograph; Optima-5 column; 30 m x 0.25 mm i.d., 0.25 μm film thickness; Supelco, Steinheim, Germany). To assess the recovery of citric acid (internal standard 1), biphenyl dicarboxylic acid was added to the samples prior to derivatization (internal standard 2). Carefully monitoring the pH avoided decomposition of citric acid during sample processing (as criticized by Schneider et al., 2010); the recovery of the first internal standard ranged between 70 and 95%. We discuss the carbon content of BPCA (BPCA-C) corrected for loss during sample preparation via internal standard 1 and normalized to charcoal [g BPCA-C per kg combustion residue] or normalized to C_{org} [g BPCA-C per kg C_{org}].

2.4.4. Spectroscopic analysis

A Bruker Tensor 27 instrument equipped with an automated high throughput device (Bruker HTS-XT) operating with a liquid N_2 cooled mercury–cadmium telluride (MCT) detector was used. Employing a broadband KBr beam splitter, spectra from 8000–600 cm^{-1} were recorded in a single run at a resolution of 4 cm^{-1} (Bornemann et al., 2008). Each analysis was performed in quintuplicate with 120 scans.

260 *2.5. Statistical analysis*

261 Data were tested for significant differences with SIGMAPLOT 11.0. One
262 Way Anova was used if parameters passed Normality-Test (Shapiro-Wilk); if
263 this test failed, Anova on Ranks values were calculated with Kruskal-
264 Wallis-*H* Test (comparison of a couple of groups) or Mann-Whitney Rank
265 Sum Test (comparison of two groups).

266

267 **3. Results**

268 *3.1. Literature survey and data analysis of fire regimes*

269 Evaluating quantitative records of fire events revealed a large range of fire
270 temperature, with the lowest value around 80 °C for grass fires (Stinson and
271 Wright, 1969; Ramsey and Oxley, 1996), but up to 950 °C for domestic fires
272 (Wells, 1960). The temperature for forest ground and shrub fires lay in
273 between this range (Table 2, Table1-SI). In general, surface fires of grass,
274 litter and herbaceous material burned at < 350 °C (Albini, 1993; Stocks and
275 Kauffman, 1997; Scott, 2000). A typical temperature for natural wild fires
276 (e.g. shrub fires) was ca. 450 °C (Hammes et al., 2006; Turney et al., 2006;
277 Alexis et al., 2007), close to the median of 503 °C calculated from literature
278 data (Table 2). For forest ground fires, a median temperature of close to 300
279 °C could be calculated (Table 2, Table 1-SI). This is in line with forest
280 ground fire temperatures found by Rundel (1983). Domestic fires, due to the
281 continuous feeding with fuel, reached the highest temperature of, on

282 average, 797 °C (Table 2, Table 1-SI; Livingstone Smith, 2001). Hence, it
283 seems reasonable to distinguish different fire regimes on the basis of both
284 combustion temperature and fuel source.
285 We produced BC calibration material from different combustion
286 temperatures and fuel sources (experiments A-C). We first evaluated their
287 chemical properties and then compared the findings with charcoal analysis
288 from a variety of natural fires.

289 *3.2. Production of BC calibration material*

290 Mass loss, C_{org} and BC content increased systematically with combustion
291 temperature in the tube furnace combustion experiments (Table 2-SI). This
292 may be interpreted as a successful production of BC calibration material
293 and allowed further discrimination of geochemical proxies for (i) duration,
294 (ii) temperature and (iii) fuel type.

295 The results from experiments A and B, including differing heating rate (5
296 °C, 10 °C min^{-1}) and duration (30 min to 12 h; Table 1) showed that,
297 irrespective of combustion temperature, the duration had no significant
298 effect on any of the charcoal properties studied (Table 2-SI; example in Fig.
299 1 via BPCA-C content of all sampling materials). Also, the BPCA pattern,
300 indicated by the ratio of penta- to hexacarboxylic benzoic acids
301 (B5CA/B6CA) and the element ratios from Rock Eval pyrolysis were not
302 related to the duration of combustion (minimum $p = 0.406$ for B5CA/B6CA,
303 OI, HI, C/N; Kruskal-Wallis *H*-test; Table 2-SI). Hence, with respect to

304 interpretation of fire regimes from geochemical properties of charcoal, the
305 effects of different fire duration on charcoal properties may be neglected.

306 *3.3. C and N concentration in BC calibration material and natural charcoal*

307 Before combustion in the tube furnace, the different fuels exhibited similar
308 C_{org} concentration (447.4 to 464.8 C mg g^{-1}). After wood combustion in
309 experiments A (domestic fires), B (slash and burn fires) and C
310 (thermosequence), the C_{org} content in the residue increased from 620 mg g^{-1}
311 at 300 °C to > 800 mg g^{-1} at 600 °C (Table 2a-SI). Residue from burned grass
312 generally exhibited lower C_{org} content (from 330 mg g^{-1} to 650 mg g^{-1}, Fig.
313 2a) than the residue from the other fuel types. Hence, it was possible to
314 distinguish the laboratory-produced wood and grass charcoal with
315 reasonable accuracy on the basis of C_{org} content (Fig. 2a).
316 The N content of fuel varied widely before combustion (1.8 to 14.8 mg g^{-1})
317 but was not systematically affected by combustion temperature. The final
318 range spanned from 2.3 to 22.1 mg N g^{-1} charcoal. The values did not allow
319 differentiation of grass charcoal from wood charcoal, but did allow to a
320 certain degree distinguishing among apple, whitethorn and beech
321 hardwoods (Fig. 2a; Table 2a-SI) as shown by a Kruskal-Wallis *H* Test
322 ($p < 0.001$). Hence, plotting C content vs. N content enabled initial
323 differentiation of charcoal origin (Fig. 2a).

324 The content of C_{org} in charcoal residue from natural fires ranged between 65
325 and 873 mg C g^{-1}. Charcoal from forest ground and domestic fires exhibited

466 to 873 mg C g^{-1}, without showing a significant difference for particles < 10 cm and < 2 cm. Grass-derived charcoal showed the lowest values (66 to 446 mg C_{org} g^{-1}), except for one outlier (697 mg C_{org} g^{-1}; Table 2b-SI). Hence, the analysis of natural charcoal samples confirmed that it is possible to differentiate charcoal derived from grass and wood derived on the basis of C_{org} content; however, in comparison with the charcoal from the BC calibration material, we observed this difference at 470 mg C_{org} g^{-1} and not at 600-650 mg C_{org} g^{-1} (Fig. 2a, dashed lines). This bias towards lower C_{org} content in natural charcoal samples (Fig. 2b) vs. the laboratory ones may result from dilution with inorganic material, e.g. ash. We tried to wash the samples with HCl (2M, overnight) to remove at least acid soluble ash. For some charcoal samples the difference in element content from the lab-produced charcoal samples disappeared, but for others the bias remained. Apparently, some of the minerals in natural charcoal cannot be easily washed out, and other procedures, such as HF treatment) might be required to get rid of the ash.

The N content of the wood-derived charcoal produced under natural fire conditions ranged between 1.3 mg N g^{-1} and 24 mg N g^{-1} (one outlier at 35 mg g^{-1}; Table 2b-SI). Plotting N content vs. C content of the natural samples confirmed a differentiation of fuel type at the above-mentioned bias (Fig. 2b).

3.4. Rock Eval parameters (OI, HI and T_{max}) in BC calibration material and natural charcoals

The HI as an indirect measurement for hydrocarbon content differed widely in the BC calibration material as a function of fuel type: for low temperature charcoal (300 °C) from einkorn, emmer and pine wood, HI values > 100 were observed, whereas the samples produced from apple and whitethorn exhibited HI values < 50. The beech charcoal had a HI value of ca. 16. Overall, values decreased as combustion temperature increased (r^2 0.57), finally reaching values of < 1 for wood charcoal and < 7 for grass charcoal at a temperature exceeding 500 °C (Fig. 3a).

The proportion of O containing organic matter (OI) behaved similarly to HI values. For low temperature charcoal, the highest OI values were observed for grass (ca. 200), whereas those for pine, apple and whitethorn averaged around 35. With increase in combustion temperature, a decline in OI values almost paralleled that of HI values for all BC calibration materials. Hence, plotting HI vs. OI enables differentiation of combustion temperature (Fig. 3a). The plot revealed trend lines that exhibited a slightly different slope for wood charcoal (black line) than for grass charcoal (grey line; Fig. 3a).

Accordingly, T_{max} revealed good correlation with temperature of combustion (r^2 0.88; Fig. 4). All charcoal produced at 600 °C and 700 °C had T_{max} > 550 °C, except for two outliers from beech charcoal combusted at 600 °C (T_{max} 380 °C). Thus, T_{max} was also a useful proxy for combustion temperature and was insensitive to fuel origin.

The HI and OI also decreased systematically for natural samples from forest ground fires to domestic fires (Fig. 3b; Table 2, Table 1-SI). Including the

range of combustion temperature depicted from the HI/OI relationship for BC calibration materials (Fig. 3a) into a HI/OI plot for natural fire samples confirmed our temperature evaluation from literature data. It had suggested that the temperature of grass and forest ground fires hardly exceeded 410 °C, whereas it typically exceeded 500 °C for domestic fires (Table 2; Fig. 3b).

The T_{max} data for charcoal from natural fire events corroborated the HI and OI findings. Charcoal from forest ground fires (literature range 120 °C to 621 °C) had a T_{max} value of 369 °C, with one outstanding value of 488 °C for the slash pile sample (i.e. only slightly above the temperature depicted from the HI/OI plots and literature data evaluation). T_{max} for grass fires exhibited values from 345 °C to 425 °C and do thus also plotted almost exactly in the median range for grass fires calculated from the HI/OI plot (Fig. 3b) and literature data (150 °C – 412 °C; Table 2, Fig. 4). The T_{max} value for domestic fires with characteristic fire temperature > 632 °C could not be recorded with our analytical Rock Eval device due to the analytical restriction (550 °C maximum).

3.5. BPCAs and MIRS as markers for charcoal amount and quality

The concentration of BPCA-C in the BC calibration material increased systematically with increasing combustion temperature (experiment C). For pine wood residue, for instance, an increase from 300 to 600 °C raised BPCA proportion from 59 to 178 g BPCA-C kg^{-1} (r^2 0.80; Table 3a-SI). For grass BC, the rise was less pronounced, ranging from 4 to 118 g BPCA-C kg^{-1} (r^2

0.54; Table 3a-SI). This rise was, however, accompanied by an overall weight loss for all wood and grass species of ca. 75% (Table 2a-SI).

In general, a higher energy input during charring results in a higher degree of BC condensation. Indeed, low temperature charcoal samples predominantly afforded benzene rings with four and five carboxyl groups (about 35% each of B4CA and B5CA at 300 °C), while high temperature charcoal afforded a significantly higher proportion of mellitic acid (40 to 50% B6CA at 600 °C; Table 3a-SI). Hence, B5CA/B6CA ratio values in the BC calibration material samples (thermosequence) correlated linearly with combustion temperature (r^2 0.88; Fig. 5). However, the ratio did not show a linear relationship to OI, but responded more sensitively when combustion temperature was > 400 °C, and remained fairly constant for cooler charring (Fig 6). Moreover, BPCA composition was also not affected by the type of fuel (Fig. 5). As much as different fire regimes can be discriminated by the specific combustion temperature (Table 2, Table 1-SI), our current data indicate that a B5CA/B6CA ratio of ca. 1.5 – 2.0 could be typical for forest ground and grass fires and 0.8-1.7 for shrub fires. In contrast, B5CA/B6CA < 0.8 should discriminate domestic fires from other fire regimes (Fig. 5).

The different B5CA/B6CA ratios values indicated structural differences in the charcoals, which might be even better revealed via MIR spectroscopy, which was therefore used. The MIR spectra of the BC calibration material samples changed systematically with increasing combustion temperature (Fig. 7). Up to 450 °C the charcoal showed a characteristic signal at 2900

418 cm^{-1} indicating aliphatic CH and CH_2 groups (Stevenson, 1994; Tatzber et
419 al., 2007). At higher combustion temperature it was absent. Then, signals
420 around 3050 cm^{-1} were observed, which are typical for aromatic groups
421 (Tatzber et al., 2007). Resolution was best for the middle temperature range
422 (450-500 °C). The C-O stretch from COOH at 1720 cm^{-1} (Stevenson, 1994)
423 was strong at low combustion temperature but disappeared at very high
424 temperature. The BC produced at 700 °C absorbed the mid infrared light
425 almost completely (Fig. 7; Roth et al., 2012). Again, these changes in MIRS
426 were not affected by variation in fuel type, corroborating the BPCA results.
427 When applying both BCPA analysis and MIRS to the charcoals sampled
428 from natural fires, we could confirm the trends mimicked in the lab:
429 domestic fires had higher BPCA-C concentrations (150 g BPCA-C kg^{-1}) than
430 charcoal from forest ground fires and grass fires (6 to 52 g BPCA-C kg^{-1},
431 with two outliers > 100 g BPCA-C kg^{-1}; Table 3b-SI). Nevertheless, the
432 BPCA concentration in natural charcoals was slightly lower than in BC
433 calibration samples produced in the laboratory (4-118 BPCA-C kg^{-1}; Table 3-
434 SI), similar to the bias in C_{org} content (see above), which we attributed to
435 dilution with inorganic matter. However, the BPCA yield normalized to C_{org}
436 as well as the BPCA pattern should not be affected by dilution processes, i.e.
437 BPCA-C/C_{org} for natural vs. lab charcoal was 28 – 195 and 9-194 g kg^{-1}.
438 Indeed, natural charcoal mostly reflected the typical temperature range of
439 fire regimes, as deduced from the B5CA/B6CA ratio assessed in the artificial
440 combustion experiments (Fig. 8a). Besides, and in contrast to the

compilation from literature data, these data also indicated a differentiation of forest ground from grass fires: the B5CA/B6CA ranged between 1.3 and 1.9 for the forest and between 0.8 and 1.4 for the grass fires, respectively. We assume that there was minimal variability in temperature for forest ground and grass fire regimes in the sampling area, whereas the overall validity of this differentiation should be taken with care unless supported by other findings. Domestic fires revealed typical B5CA/B6CA values of 0.3 to 0.8 (Fig. 8a), clearly different from the values for the other fire regimes and significant at $p < 0.001$ level of probability.

The MIRS spectra of charcoal from natural fires finally confirmed the systematic changes attributable to different fire regimes (Fig. 8b). Aliphatic CH and CH_2 groups showed signals at 2900 cm^{-1} for forest and grass fire samples but the signal was absent from charcoal from domestic fires. This is in line with MIRS findings for BC calibration material samples at comparable temperatures. Aromatic signals around 3050 cm^{-1} were not observed for charcoal from natural grass and forest ground fires, likely due to the fact that the selected natural charcoal samples did not cover the required temperature range of 450 – 500 °C (see Fig. 3b, 7, 8b). Like the BC calibration samples, the COOH stretch at 1720 cm^{-1} was characteristic for charcoal from low temperature fires but was absent for charcoal formed at high temperature from domestic fires. Hence, the spectra nicely complemented the assignment of different combustion temperatures.

4. Discussion

464 *4.1. Fire regime*

465 Since various factors control a fire event, extracting the most relevant fire
466 properties is essential for geochemical differentiation of fire regimes. We
467 concentrated on fire duration, temperature and fuel type and on analysis of
468 charcoal as one main fire residue. We disregarded O_2 supply and wind
469 speed, assuming that the effect of these factors was included in fire duration
470 and temperature. Hence, Smith and Sparling (1966) found, for instance,
471 that higher wind speed (> 2 m sec^{-1}) may exert a "cooling effect" on fire. In
472 contrast, Fahnestock and Hare (1964) found that woody vegetation burns
473 longer than grassy vegetation, but forest headfires burn hotter because the
474 flames are fanned by the wind (Hare, 1961). There are also zones in natural
475 fires which are excluded from wind influence (e.g. tree bark). Hence, a
476 different wind speed (and thus also O_2 supply) is either negatively or
477 positively related to combustion temperature, but whatever the direction of
478 this correlation, the measured combustion temperature integrates these
479 effects.
480 Domestic fires are usually hotter than grass and forest ground fires (Cohen-
481 Ofri et al., 2006; Braadbaart and Poole, 2008; Maggetti et al., 2011), and
482 this is also reflected in our data: we found more B6CAs as a result of higher
483 fire temperature in natural charcoal collected from domestic fires than in
484 charcoal collected from ground fires (i.e. grass and forest; Fig. 8a), and a loss
485 of aliphatic moieties in the MIR spectra (Fig 8b).

In general, fire temperature is heterogeneous, e.g. forest fires burn at 800 °C at the crown (Pyne et al., 1996; Alexis et al., 2007), but at lower temperature at the ground (Scott, 2000). Detecting some variability in the characteristics of charcoal was thus also reasonable and we recommend that any fire regime reconstruction has to be conducted on a range of charcoal samples (as provided by finely dispersed, molecular scale BC on soil) and not on a single BC analysis of n=1 charcoal found. Certainly, deducing fire regimes from charcoal properties is most reliable when aerobic degradation of the char itself maybe neglected, such as in anaerobic parts of bog soil or in limnic and marine archives, respectively.

4.2. Effect of fire duration on charcoal formation

Braadbaart and Poole (2008) suggested that the mass loss of fuel during heating might be used as an indicator for the duration of combustion. They found that combustion residues of equal mass loss also have similar chemical properties, because the conversion of cellulose, hemicellulose and lignin to new compounds during heating occurs to a similar degree. Our data suggested, however, that across the heating duration times realistically tested, all BC calibration materials showed similar mass loss at a given temperature (Table 2-SI), whereas the BC amount was not significantly affected by charring duration (Fig. 1). Though at timescales < 30 min differences in BC quantity were observed previously (Glaser et al., 1998), we assume that the observed stability of the BC parameters for > 30 min combustion time more likely characterizes the majority of natural charcoal.

We relate the initial mass loss mainly to loss of moisture and volatile OM but not to formation of novel structures, which obviously requires higher input of energy (higher temperature) and less prolonged energy input at a given temperature (Braadbaart and Poole, 2008). As a result, we could disregard the effect of charring duration on our geochemical proxies.

4.3. Temperature effect on charcoal formation

Laboratory experiments suggest that physical and chemical charcoal properties depend on fire temperature (Baldock and Smernick, 2002; Brown et al., 2006; Hammes et al., 2006; Braadbaart and Poole, 2008; Schneider et al., 2010). Any formation of charcoal begins with a loss of easily oxidizable OM, which slows down between 300 and 400 °C as compatible with our HI, OI and MIRS findings (loss of aliphatic and carboxylic signal intensity; Fig. 7) and the model of Keiluweit et al. (2010). From 300 to 400 °C we observed dehydration and perhaps also demethylation via a rough decrease in HI and OI relative to the BPCA pattern (Fig. 6). MIR adsorption also indicated that in this temperature range the transformation of more stable carbon forms (lignin, cellulose) to aromatic carbon (MIR signals at 3050 and 1500 cm^{-1}; Fig. 7) began. Moreover, the curvature in B5CA/B6CA vs. OI revealed that from about 400 °C aromatization and coagulation dominated the combustion process, whereas at lower temperature only OI, but not the BPCA pattern, changed, likely reflecting loss of water and other volatiles (Fig. 6).

High temperature combustion has been known to end in nearly complete carbonization of samples in form of “turbostratic”, polyaromatic crystallites

(Keiluweit et al., 2010), respectively the graphite-like structure of a soot particle (Schmidt and Noack, 2000; Gustafsson et al., 2001). Along this line of ongoing carbonization and aromatization, McBeath et al. (2011) found that single aromatic rings are formed which condense above 400 °C. As a result, B5CA/B6CA values decreased when combustion temperature rose, as observed in the laboratory produced BC calibration materials samples (Fig. 5) and respective natural charcoal samples. They finally provided distinct classes for different fire regimes for charcoal derived from forest ground, grass and domestic fires (Fig. 8). It should be kept in mind, however, that the natural charcoal samples here all stemmed from a certain region in Serbia and Russia. The fact that these natural forest ground and grass charcoal samples could be differentiated via the B5CA/B6CA ratio, indicating a temperature difference of ca. 100 °C - whereas this temperature difference was not indicated by the literature review - may therefor be explained by reduced natural variation in combustion temperature among the fires in these regions vs. the more global average gained from the literature review (Table 2). Likewise, reconstructing fire regimes on a regional scale is more sensitive than across different regions.

Although the HI/OI ratio could be shown to be more sensitive for temperature changes < 400 °C (Fig. 6), dilution with other OM in environmental matrices would be problematic. However, the Rock Eval pyrolysis method gives, with T_{max}, another temperature sensitive parameter

554 to hand (Fig. 4, r^2 0.88), which is robust against dilution from biomass
555 derived organic carbon, e.g. in soil.

556 *4.4. Influence of fuel type*

557 Plant biomass differs in C_{org} composition mainly due to changing
558 proportions of lignin, cellulose and hemicellulose (e.g. Bridgwater et al.,
559 1999; Czimczik et al., 2002; Thevenon et al., 2010). Softwood contains the
560 highest lignin content relative to holocellulose (cellulose + hemicellulose) vs.
561 hardwood or grass, with the lowest lignin content (Sjöström, 1993; Czimczik
562 et al., 2002; Braadbaart and Poole, 2008). Additionally, holocellulose
563 degrades over a narrower temperature range than the more thermally
564 stable lignin (Bridgwater et al., 1999). Hence, lower lignin concentration in
565 grass might lead to low residual C_{org} in grass derived charcoal due to more
566 efficient combustion vs. wood, thereby facilitating differentiation of these
567 fuels (Fig. 2a).

568 However, as noted above, C_{org} content and the discrimination line for grass
569 and wood charcoal in the BC calibration materials shifted from 600 mg g^{-1}
570 C_{org} to slightly lower C_{org} content in natural charcoal (450 mg g^{-1} C_{org};
571 dashed lines in Fig. 2a and b). Hence, it still appears possible to
572 discriminate C sources, but only when one can succeed in getting rid of the
573 contamination from inorganic matter. We failed to do so with 2M HCl.
574 Testing other treatments, e.g. HF, might still warrant attention. Unless
575 solved, the validation of fuel specific markers in natural charcoals was
576 therefore unsatisfactory using simple chemical analysis (Figs. 2b, 3b).

577 *4.5 Oxygen supply*

578 It is fairly known that under inert conditions less OM is lost by oxidation to
579 CO_2, but stabilized in charcoal - a fact on which biochar production is based.
580 Comparing results from pyrolyzed wood it is apparent that C_{org} content is
581 ca. 100 mg g^{-1} higher than in our combustion experiment (Baldock and
582 Smernik, 2002; Trompowski et al., 2005; Schneider et al., 2010).
583 Additionally Kloss et al. (2009) pyrolyzed grass and wood under low O_2
584 conditions (< 1 vol %). For wood, the C_{org} content is comparable with our
585 results, indicating that our lab experiments might have been dominated by
586 O_2 deficient combustion due to an O_2 supply only to the surface of the intact
587 branches (diam. < 1 cm). However, for pyrolyzed grass the values were
588 higher than in our experiment. Hence, we suggest that, if O_2 deficiency in
589 grass fires occurs - which does not seem likely in nature due to the filigree
590 structure of grass - C_{org} concentration might be elevated. Indeed, the natural
591 grass charcoals analyzed in this study had lower C_{org} content at the
592 respective temperatures (discussed above as an effect of dilution), which
593 might be related to an elevated O_2 supply in the field. Correspondingly, we
594 could observe a deviation between B5CA/B6CA values for grass charcoal
595 calibration material and natural grass fire residues, also indicating that O_2
596 availability was not representative in the tube furnace (Fig. 8a).
597 As far as we know, the thermosequence of Schneider et al. (2010) is the only
598 work investigating the BPCA quantity and quality of pyrolyzed wood. The
599 B5CA/B6CA ratio, as a marker for BC quality, yielded results comparable to

600 the findings of our series of lab produced charcoal. Nevertheless, the
601 B5CA/B6CA valuess of Schneider et al. (2010) were lower by ca. 0.3
602 compared with the values reported in our study (equivalent to ca. + 50 °C;
603 Fig. 8), indicating a higher degree of aromatization under inert conditions.
604 Different O_2 supply therefore appears to contribute to an additional bias in
605 the source assignment of charcoal to different fire regimes; however, the
606 effect appears to be small compared with the differences induced by
607 combustion temperature.
608

609 **5. Conclusions**

610 On the basis of an evaluation of literature data and chemical analysis of
611 charcoal it is possible to reconstruct fire temperature as a proxy for different
612 fire regimes. Of the analytical methods tested, particularly the combination
613 of Rock Eval analysis with BPCA analysis and MIRS was promising in this
614 regard. Overall, as combustion temperature increased, the HI and OI
615 increased and B5CA/B6CA decreased linearly with increasing combustion
616 temperature. The fuel source had only little impact on these correlations,
617 the combustion duration having no impact. While the quantitative proxies
618 C_{org}, N, HI and OI support temperature reconstruction for pure charcoals
619 only, qualitative proxies - MIRS, T_{max} and BPCA pattern analysis - exhibit
620 potential to also work for finely dispersed charcoal residues in
621 environmental matrices. Challenging is further reduction in a slight bias

between lab produced chars and those produced in the field, likely caused by remaining differences in the content of ash formed and O_2 supply.

Acknowledgments

Special thanks go to U. Tegtmeier, Institute of Prehistoric Archaeology, University of Cologne for providing a large sample set of charcoal samples. A. Börner (Leibniz Institute of Plant Genetics and Crop Plant Research (IPK), Gatersleben, Germany) is thanked for providing einkorn and emmer grass. We thank I. Wieland for technical assistance with BPCA analysis, and M. Kasten for elemental analysis. Financial support was received from the Deutsche Forschungsgemeinschaft (German Research Council; DFG), subproject F3 of the Collaborative Research Centre 806 "Our Way to Europe - Culture-Environment Interaction and Human Mobility in the Late Quaternary" and WI2810/9-1. We thank K. Wiedner and two anonymous reviewers for helpful comments.

Supplementary material

The Supplementary material provides tables with individual fire temperatures from wildfire events (Table 1-SI) and variables and geochemical proxies for the laboratory experiments (Table 2a-SI, Table 3a-SI) and natural charcoals (Table 2b-SI, Table 3b-SI).

Associate Editor – **S. Derenne**

644 **References**

645 Albini, F.A., 1993. Dynamics and modeling vegetation fires: observations.
646 In: Crutzen, P.J., Goldammer, J.G. (Eds.), Fire in the Environment: the
647 Ecological, Atmosheric and Climatic Importance of Vegetation Fires.
648 Wiley, Chichester, pp. 39-52.
649 Alexis, M.A., Rasse, D.P., Rumpel, C., Bardoux, G., Péchot, N., Schmalzer,
650 P., Drake, B., Mariotti, A., 2007. Fire impact on C and N losses and
651 charcoal production in a scrub oak ecosystem. Biogeochemistry 82, 201-
652 216.
653 Almendros, G., Knicker, H., González-Vila, F.J., 2003. Rearrangement of
654 carbon and nitrogen forms in peat after progressive thermal oxidation as
655 determined by solid-state ^{13}C- and ^{15}N-NMR spectroscopy. Organic
656 Geochemistry 34, 1559-1568.
657 Antal Jr., M.J. and Grønli. M. 2003: The art, science, and technology of
658 charcoal production. Industrial & Engineering Chemistry Research 42,
659 1619-1640.
660 Apaydin-Varol, E., Pütün, E., Pütün, A.E., 2007. Slow pyrolysis of pistachio
661 shell. Fuel 86, 1892-1899.
662 Archibold, O.W., Nelson, L. J., Ripley, E., A., Delanoy, L. 1998. Fire
663 temperatures in plant communities of the Northern Mixed Prairie.
664 Canadian Field-Naturalist 112, 234-240.
665 Bailey, A.W., Anderson, M.L., 1980. Fire temperatures in grass, shrub and
666 aspen forest communities of Central Alberta. Journal of Range
667 Management 33, 37-40.
668 Baldock, J.A., Smernik, R.J., 2002. Chemical composition and bioavailability
669 of thermally, altered *Pinus resinosa* (Red Pine) wood. Organic
670 Geochemistry 33, 1093–1109.
671 Beadle, N.C.W., 1940. Soil temperatures during forest fires and their effect
672 on the survival of vegetation. Journal of Ecology 28, 180-192.
673 Beaumont, E. (Ed.), 1985. Industrial Charcoal Making. FAO Forestry Paper,
674 vol. 63. Food and Agricultural Organization of the United Nations, Rome
675 (http://www.fao.org/docrep/X5555E/x5555e00.htm#Contents).
676 Bently, J. and Fenner, R.L., 1958. Soil temperatures during burning related
677 to postfire seedbeds on woodland range. Journal of Forestry 56, 737-740.
678 Bordenave, M.L., Espitalié, J., Leplat,P., Oudin, J.L.,Vandenbroucke, M.,
679 1993. Screening techniques for source rock evaluation. In: Bordenave,
680 M.L. (Ed.), Applied Petroleum Geochemistry. Éditions Technip, Paris,
681 pp. 219-278.
682 Bornemann, L., Welp, G., Brodowski, S., Rodionov, A., Amelung, W., 2008.
683 Rapid assessment of black carbon in soil organic matter using mid-
684 infrared spectroscopy. Organic Geochemistry 39, 1537-1544.
685 Braadbaart, F. and Poole, I., 2008. Morphological, chemical and physical
686 changes during charcoalification of wood and its relevance to
687 archaeological contexts. Journal of Archaeological Science 35, 2434-2445.

688 Bridgwater, A.V., Meier, D., Radlein, D., 1999. An overview of fast pyrolysis
689 of biomass. Organic Geochemistry 30, 1479-1493.
690 Brodowski, S., Amelung, W., Haumaier, L., Abetz, C., Zech, W., 2005a:
691 Morphological and chemical properties of black carbon in physical soil
692 fractions as revealed by scanning electron microscopy and energy-
693 dispersive X-ray spectroscopy. Geoderma128: 116-129.
694 Brodowski, S., Rodionov, A., Haumaier, L., Glaser, B., Amelung, W., 2005b.
695 Revised black carbon assessment using benzene polycarboxylic acids.
696 Organic Geochemistry 36, 1299-1310.
697 Brodowski, S., John, B., Flessa, H., Amelung, W., 2006: Aggregate-occluded
698 black carbon in soil. European Journal of Soil Science 57, 539-546.
699 Brown, R.A., Kercher, A.K., Nguyen, T.H., Nagle, D.C., Ball, W.P., 2006.
700 Production and characterization of synthetic wood chars for use as
701 surrogates for natural sorbents. Organic Geochemistry 37, 321–333.
702 Busse, M.D., Hubbert, K.R., Fiddler, G.O., Shestak, C.J., Powers, R.F., 2005.
703 Lethal soil temperatures during burning of masticated forest residues.
704 International Journal of Wildland Fire 14, 267-276.
705 Cohen-Ofri, I., Weiner, L., Boaretto, E., Mintz, G., Weiner, S., 2006. Modern
706 and fossil charcoal: aspects of structure and diagenesis. Journal of
707 Archaeological Science 33, 428-439.
708 Countryman, C.M., 1964. Mass Fires and Fire Behavior. Forest Service,
709 U.S. Department of Agriculture, Pacific Southwest Forest and Range
710 Experiment Station, 53 pp.
711 Czimczik, C.I., Preston, C.M., Schmidt, M.W.I., Werner, R.A., Schulze, E.-
712 D., 2002. Effects of charring on mass, organic carbon, and stable carbon
713 isotope composition of wood. Organic Geochemistry 33, 1207-1223.
714 Dupuy, J.-L., Vachet, P., Maréchal, J., Meléndes, J., Castro de, A.J., 2007.
715 Thermal infrared emission–transmission measurements in flames from a
716 cylindrical forest fuel burner. International Journal of Wildland Fire 16,
717 324-340.
718 Espitalié, J., Laporte, J.L., Madec, M., Marquis, F., Leplat, P., Paulet, J.,
719 Boutefeu, A., 1977. Méthode rapide de caractérisation des roches mères,
720 de leur potential pétrolier et de leur degré d'evolution. Rock
721 Evalpyrolysis and its applications. Revue de l'Institut Francais du
722 Pétrole 32, 23-42.
723 Espitalié, J., Deroo, G., Marquis, F., 1985. Rock Eval pyrolysis and its
724 applications.Revue de l'Institut Francais du Pétrole Part I 40, 653–578,
725 Part II 40, 755– 784, Part III 41, 73– 89.
726 Fahnestock, G.R. and Hare, R.C., 1964. Heating of tree trunks in surface
727 fires. Journal of Forestry 62, 799-805.
728 Fierro, A., Rutigliano, F.A., Marco de, A., Castaldi, S., Virzo de Santo, A.,
729 2007. Post-fire stimulation of soil biogenic emission of CO_2 in a sandy soil
730 of a Mediterranean shrubland. International Journal of Wildland Fire
731 16, 573-583.

732 Fraser, J.F., Choo, K.L., Sutch, D., Kimble, R.M., 2003. The morning after
733 the night before: campfires revisited. Medical Journal of Australia 178,
734 30.
735 Gibson, A., Wood, A., 1997. Prehistoric Pottery for the Archaeologist, 2nd ed.
736 Leicester University Press, London and Washington, pp. 336.
737 Glaser, B., Haumaier, L., Guggenberger, G., Zech, W., 1998. Black carbon in
738 soils: the use of benzenecarboxylic acids as specific markers. Organic
739 Geochemistry 29, 811-819.
740 Goldberg, E. D., 1985. Black Carbon in the Environment. Wiley, New York.
741 Grasby, S.E., Sanei, H., Beauchamp, B., 2011. Catastrophic dispersion of
742 coal fly-ash into oceans during the latest Permian extinction. Nature
743 Geoscience 4, 104–107, doi:10.1038/ngeo1069.
744 Gustafsson, Ö., Bucheli, T.D., Kukulska, Z., Andersson, M., Largeau, C.,
745 Rouzaud, J.N., Reddy, C.M., Eglinton, T.I., 2001. Evaluation of a protocol
746 for the quantification of black carbon in sediments. Global
747 Biogeochemical Cycles 15, 881-890.
748 Hammes, K., Smernik, R.J., Skjemstad, J.O., Herzog, A., Vogt, U.F.,
749 Schmidt, M.W.I., 2006. Synthesis and characterisation of laboratory-
750 charred grass straw (*Oryza sativa*) and chestnut wood (*Castanea sativa*)
751 as reference materials for black carbon quantification. Organic
752 Geochemistry 37, 1629-1633.
753 Hammes, K., Schmidt, M.W.I., Smernik, R.J., Currie, L.A., Ball, W.P.,
754 Nguyen, T.H., Louchouarn, P., Houel, S., Gustafsson, Ö., Elmquist, M.,
755 Cornelissen, G., Skjemstad, J.O., Masiello, C.A., Song, J., Peng, P.,
756 Mitra, S., Dunn, J.C., Hatcher, P.G., Hockaday, W.C., Smith, D.M.,
757 Hartkopf- Fröder, C., Böhmer, A., Lüer, B., Huebert, B.J., Amelung, W.,
758 Brodowski, S., Huang, L., Zhang, W., Gschwend, P.M., Flores-Cervantes,
759 D.X., Largeau, C., Rouzaud, J.-N., Rumpel, C., Guggenberger, G., Kaiser,
760 K., Rodionov, A., Gonzalez-Vila, F.J., Gonzalez-Perez, J.A., de la Rosa,
761 J.M., Manning, D.A.C., López-Capél, E., Ding, L., 2007. Comparison of
762 black carbon quantification methods using reference materials from soil,
763 water, sediment and the atmosphere, and implications for the global
764 carbon cycle. Global Biogeochemical Cycles 21, 2-18.
765 Hammes, K., Smernik, R.J., Skjemstad, J.O., Schmidt, M.W.I., 2008.
766 Characterisation and evaluation of reference materials for black carbon
767 analysis using elemental composition colour, BET surface area and ^{13}C
768 NMR spectroscopy. Applied Geochemistry 23, 2113-2122.
769 Hare, R. C. 1961. Heat Effects on Living Plants. U.S. Department of
770 Agriculture 183, 32 pp.
771 Haumaier, L., Zech, W., 1995. Black carbon – possible source of highly
772 aromatic components of soil humic acids. Organic Geochemistry 23, 191-
773 196.
774 Hobbs, R.J., Gimingham, C.H., 1984. Studies on fire in Scottish heathland
775 communities: I. Fire characteristics. Journal of Ecology, 72, 223-240.

776 Ito, M., Iizumi, S., 1960. Temperatures during grassland fires and their
777 effect on some species in Kawatabi, Miyagi Prefecture. Science Reports of
778 the Research Institutes, Tohoku University - Series D 11, 109-114.
779 Keeley, J.E., McGinnis, T.W., 2007. Impact of prescribed fire and other
780 factors on cheatgrass persistence in a Sierra Nevada ponderosa pine
781 forest. International Journal of Wildland Fire 16, 96-106.
782 Keiluweit, M., Nico, P.S., Johnson, M.G., Kleber, M., 2010. Dynamic
783 molecular structure of plant biomass-derived black carbon (biochar).
784 Environmental Science and Technology 44, 1247-1253.
785 Kenworthy, J. B. 1963. Temperatures in heather burning. Nature 200, 1226.
786 Kloss, S., Zehetner, F., Dellantonio, A., Hamid, R., Ottner, F., Liedtke, V.,
787 Schwanninger, M., Gerzabek, M.H., Soja, G., 2011. Characterization of
788 slow pyrolysis biochars: effects of feedstocks and pyroylsis temperature
789 on biochar properties. Journal of Environmental Quality 41, 990-1000.
790 Knicker, H., 2011. Pyrogenic organic matter in soil: Its origin and
791 occurrence, its chemistry and survival in soil environments. Quaternary
792 International 243, 251-263.
793 Knörzer, K.K., Gerlach, R., Meurers-Balke, J., Kalis, A.J., Tegtmeier, U.,
794 Becker, W.D., Jürgens, A., 1999. Pflanzenspuren. Archäobotanik im
795 Rheinland: Agrarlandschaft und Nutzpflanzen im Wandel der Zeit.-
796 Materialien zur Bodendenkmalpflege im Rheinland, H. 10; Köln
797 (Rheinland-Verlag).
798 Livingstone Smith, A., 2001. Bonfire II: The return of pottery firing
799 temperatures. Journal of Archaeological Science 28, 991-1003.
800 Maggetti, M., Neururer, Ch., Ramseyer, D., 2011: Temperature evolution
801 inside a pot during experimental surface (bonfire) firing. Applied Clay
802 Science 53, 500-508.
803 Martineau, R., Pétrequin, P., 2000. La cuisson des poteries néolithiques de
804 Chalain (Jura), approche expérimentale et analyse archéologique. In:
805 Pétrequin, P., Thiriot, J., Benoit, P. (Eds.), Arts du Feu et Productions
806 Artisanales. XXe Rencontres Internationales d'Archéologie et d'Histoire
807 d'Antibes, Editions APDCA, Antibes, pp. 337–358.
808 Masiello, C.A., Druffel, E.R.M., 1998. Black carbon in deep-sea sediments.
809 Science 280, 1911-1913.
810 Massman, W.J., Frank, J.M., Reisch, N.B., 2008. Long-term impacts of
811 prescribed burns on soil thermal conductivity and soil heating at a
812 Colorado Rocky Mountain site: a data/model fusion study. International
813 Journal of Wildland Fire 17, 131-146.
814 McBeath, A.V., Smernik, R.J., Schneider, M.P.W., Schmidt, M.W.I., Plant,
815 E.L., 2011. Determination of the aromaticity and the degree of aromatic
816 condensation of a thermosequence of wood charcoal using NMR. Organic
817 Geochemistry 42, 1194-1202.
818 McKell, C. M., Wilson, A. M., Kay, B. L., 1962. Effective burning of
819 rangelands infested with medusahead. Weeds 10, 125-131.

820 Miller, R.B., Stout, J.D., Lee, K.E., 1955. Biological and chemical changes
821 following scrub burning on a New Zealand hill soil. New Zealand Journal
822 of Science and Technology 37, 290-313.
823 Misra, M.K., Ragland, K.W., Baker, A.J., 1993. Wood ash composition as a
824 function of furnace temperature. Biomass and Bioenergy 4, 103-116.
825 Neary, D.G., Klopatek, C.C., DeBano, L.F., Ffolliott, P.F., 1999. Fire effects
826 on belowground sustainability: a review and synthesis. Forest Ecology
827 and Management 122, 51-71.
828 Novakov, T., 1984. The role of soot and primary oxidants in atmospheric
829 chemistry. The Science of the Total Environment 36, 1-10.
830 Preston, M.C., Schmidt, M.W.I., 2006. Black (pyrogenic) carbon: a synthesis
831 of current knowledge and uncertainties with special consideration of
832 boreal regions. Biogeoscience 3, 397-420.
833 Pyne, S.J., Andrews, P.L., Laven, R.D., 1996. Introduction to Wildland Fire.
834 Second ed. John Wiley and Sons, Inc., New York.
835 Ramsay, P.M., Oxley, E.R.B., 1996. Fire temperatures and postfire plant
836 community dynamics in Ecuadorian grass páramo. Vegetation 124, 129-
837 144.
838 Roth, P.J., Lehndorff, E., Brodowski, S., Bornemann, L., Sanchez-Garcia. L.,
839 Gustafsson, Ö., Amelung, W., 2012. Differentiation of black carbon pools
840 in soils: Method comparisons and perspectives. Organic Geochemistry 46,
841 66-75.
842 Rowlett, R. M., Mandeville, M. D., Zeller, E. J, 1974. The interpretation and
843 dating of humanly worked siliceous materials by thermoluminescent
844 analysis. Proceedings of the Prehistoric Society 40, 3744.
845 Rundel, P.W., 1983. Impact of fire on nutrient cycles in Mediterranean-type
846 ecosystems with reference to chaparral. In: Kruger, F.J., Mitchell, D.T.,
847 Jarvis, J.U.M. (Eds.), Mediterranean-Type Ecosystems: The Role of
848 Nutrients, Springer-Verlag, New York, NY, pp. 192-2207.
849 Sackett, S.S., Haase, S.M., 1992. Measuring Soil and Tree Temperatures
850 During Prescribed Fires with Thermocouple Probes. USDA Forest
851 Service General Technical Report PSW-GTR-131 PSW-131.
852 Sah, J.P., Ross, M.S., Snyder, J.R., Koptur, S., Cooley, H.C., 2006. Fuel
853 loads, fire regimes, and post-fire fuel dynamics in Florida Keys pine
854 forest. International Journal of Wildland Fire 15, 463-478.
855 Sampson, A. W. 1944. Plant succession on burned chaparral lands in
856 northern California. University of California Agricultural Experiment
857 Station, Berkeley, CA., Bulletin 685, p. 144.
858 Schmidt, M.W.I., Noack, A.G., 2000. Black carbon in soils and sediments:
859 analysis, distribution, implications, and current challenges. Global
860 Biogeochemical Cycles 14, 777–793.
861 Schneider, M.P.W., Hilf, M., Vogt, U.F., Schmidt, M.W.I., 2010. The benzene
862 polycarboxylic acid (BPCA) pattern of wood pyrolyzed between 200 °C
863 and 1000 °C. Organic Geochemistry 41, 1082-1088.
864 Scott, A.C., 2000. The Pre-Quaternary history of fire. Palaeogeography,
865 Palaeoclimatology, Palaeoecology 164, 281-329.

Shepard, A.O., 1956. Ceramics for the Archaeologist. Publication 609. Washington, D.C.: Carnegie Institution of Washington.

Sjöström, E., 1993. Wood Chemistry: Fundamentals and Applications. Second Edition, Academic Press, San Diego, 293 pp.

Smith, D.W., Sparling, J.H., 1966. The temperatures of surface fires in jack pine barren: I. The variation in temperatures with time. Canadian Journal of Botany 44, 1285- 1292.

Stevenson, F.J., 1994. Humus Chemistry. Genesis, Composition, Reactions John Wiley and Sons, Inc., New York, 512 pp.

Stinson, K.J., Wright, H.A., 1969. Temperatures of headfires in the southern mixed prairie of Texas. Journal of Range Management 22, 169-174.

Stocks, B.J., Kauffmann, J.B., 1997. Biomass consumption and behavior of wildland fires in boreal, temperate and tropical ecosystems: parameters necessary to interpret historic fire regimes and future fire scenarios. In: Clak, J.S., Cachier, H., Goldammer, J.G., Stocks, B. (Eds.), Sediment records of Biomass Burning and Global Change, NATO ASI Series vol. I 51. Sringer, Berlin, pp. 169-188.

Tatzber, M., Stemmer, M., Splegel, H., Katziberger, C., Haberhauer, G., Mentler, A., Gerzabek, M.H., 2007. FTIR-spectroscopic characterization of humic acids and humin fractions obtained by advanced NaOH, $Na_4P_2O_7$, and Na_2CO_3 extraction procedures. Journal of Plant Nutrition and Soil Science 170, 522-529.

Thevenon, F., Williamson, D., Bard, E., Anselmetti, F.S., Neaufort, L., Cachier, H., 2010. Combining charcoal and elemental black carbon analysis in sedimentary archives: Implications for past fire regimes, the pyrogenic carbon cycle, and the human–climate interactions. Global and Planetary Change 72, 381-389.

Trompowsky, P.M., Benites, V.D.M., Madari, B.E., Pimenta, A.S., Hockaday, W.C., Hatcher, P.G., 2005. Characterization of humic like substances obtained by chemical oxidation of eucalyptus charcoal. Organic Geochemistry 36, 1480-1489.

Turney, C.S.M., Wheeler, D., Chivas, A.R., 2006. Carbon isotopic fractionation in wood during carbonization.Geochimica et Cosmochimica Acta 70, 960–964.

Tylecote, R. F., 1962. Metallurgy in Archaeology. Arnold Press, London, UK.

van Krevelen, D.W., 1950. Graphical-statistical method for the study of structure and reaction processes of coal. Fuel 29, 269–284.

Wanthongchai, K., Bauhus, J., Goldammer, J.G., 2008. Nutrient losses through prescribed burning of above ground litter and understory in dry dipterocarp forests of different fire history.Catena 74, 321-332.

Wells, C., 1960. A study of cremation. Antiquity 34, 29-37.

Whittaker, E., 1961. Temperatures in heath fires. Journal of Ecology 49, 709-715.

Ziolkowski, L.A., Chamberlin, A.R., Greaves, J., Druffel, E.R.M, 2011. Quantification of black carbon in marine systems using the benzene

polycarboxylic acid method: a mechanistic and yield study. Limnology and Oceanography - Methods 9, 140-149.

Table and Figure Captions

Table 1

Setups for production of BC calibration material chosen with respect to typical fire regime variables: temperature, heating rate and duration, applied to different fuels.

Table 2

Data from literature survey (SD, standard deviation; n.d., not detectable).[a] [a] Range and median of wind speed and temperature were calculated from average fire recordings (temperature measurement was at ground level to a maximum 15 cm above ground; for detailed information see Table 1-SI.

Editor: text in yellow should be a footnote to the table

Fig. 1

Combustion duration shows no significant impact on char formation as shown by example here for BPCA-C amount ($p > 0.05$).

Fig. 2

C_{org} and N concentration of grass and wood charcoal for a) BC calibration materials. A distinct discrimination of grass charcoal from wood charcoal via C_{org} content is obvious, while variation in N content provides to some degree differentiation of fuel type (shaded grey bars; open symbols indicate C_{org} and

936 N content of respective unburned fuels); b) charcoal from natural fire
937 regimes can be differentiated according to prevalent fuel type via C_{org} and N
938 content. A systematic shift to lower C_{org} is related to dilution by inorganic
939 matter.
940
941 **Fig. 3**
942 Change in OI and HI vs. temperature in a) BC calibration materials. The
943 offset between OI and HI can be attributed to difference in fuel type [see
944 trend lines for grass (grey) and wood (black)]; (b) shows discrimination of
945 charcoal from natural fires via HI and OI. Temperature ranges were taken
946 from laboratory-controlled combustion experiments A, B and C (Fig. 3a) and
947 translated to the charcoals formed under natural fire conditions.
948
949 **Fig. 4**
950 T_{max} of a) laboratory produced charcoal vs. combustion temperature. T_{max} is
951 close to a one-to-one correlation with temperature but has a fixed positive
952 offset of ca. 50 °C; b) shows T_{max} analysis of natural charcoal samples and
953 demonstrates that T_{max} for charcoals from forest ground, grass, and
954 domestic combustion fits with the respective typical temperature ranges for
955 laboratory experiments and the literature review (outlier sample from slash
956 pile in brackets).
957
958 **Fig. 5**

Relationship between B5CA/B6CA and and combustion temperature. The figure shows that this ratio declines as combustion temperature increases, irrespective of the fuel source used for charcoal production (r^2 0.88; $p<$ 0.001). Temperature ranges depicted for typical fire regimes were from the literature review.

Fig. 6

Correlating temperature sensitive B5CA/B6CA ratio vs. OI reveals a non-linear but systematic behaviour related to two phases of the combustion process: dehydration to 400 °C and subsequent aromatization.

Fig. 7

MIRS characterization of charred apple wood, combusted from 300 °C to 700 °C. The signal response differed with increasing heat treatment. Solid lines indicate bonds typical of aromatic compounds, dotted lines aliphatic CH and CH_2 groups, and medium dashed lines C-O stretch of COOH.

Fig. 8

Fig. 8a: Range of B5/B6CA ratios in natural charcoals as put into context with (i) fire regime and ii) as related to observations from BC calibration materials (dotted regression line from Fig. 5). Natural residues of forest and domestic fires fitted well to calibration materials, while charred grass separated more clearly from forest fires than indicated by the literature

survey; (b) MIR spectra of charcoal from natural fires revealed comparable dealkylation and aromatization trends as for laboratory produced charcoal (Fig. 7; outlier sample from slash pile in brackets).

Figure1

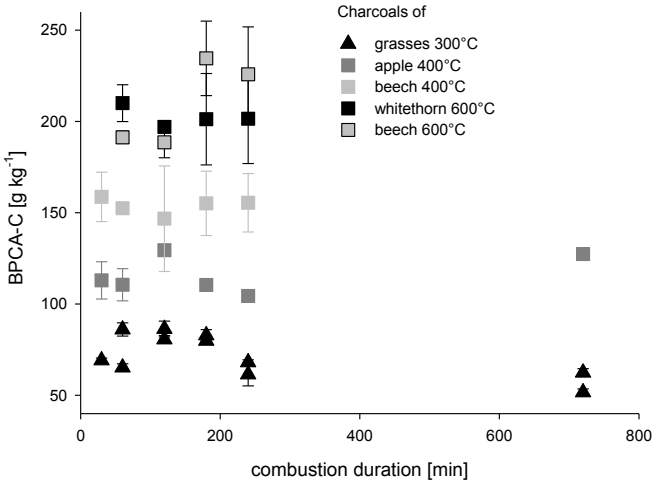


Figure 1

Figure2

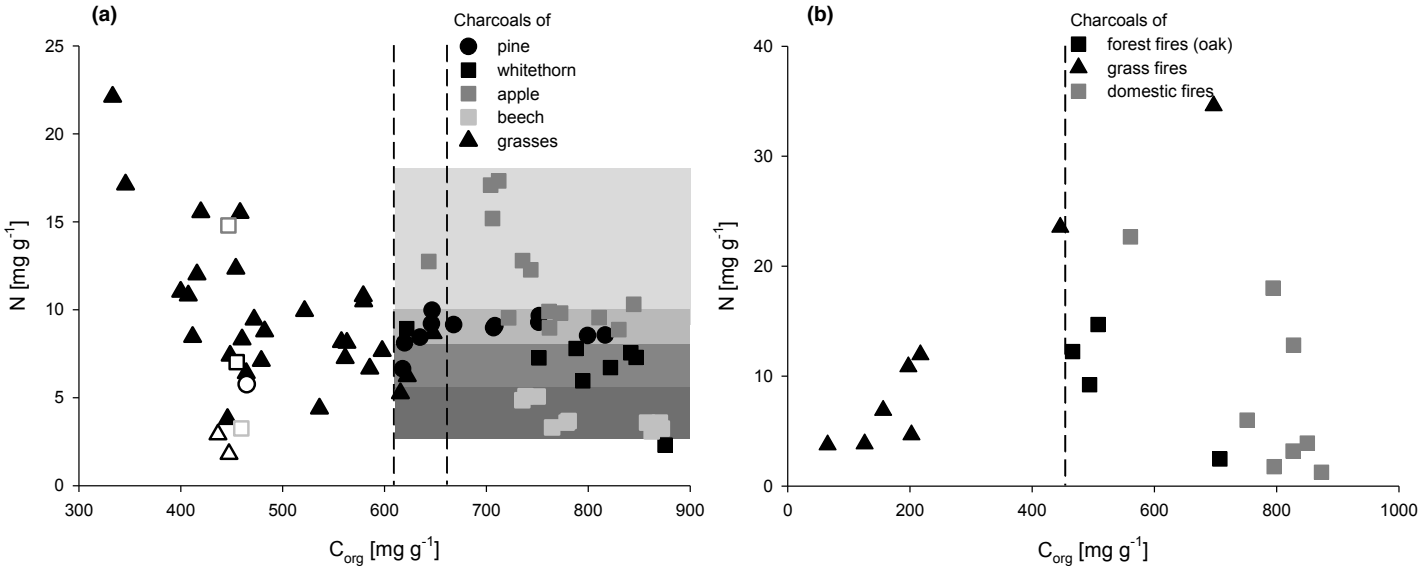


Figure 2

Figure3

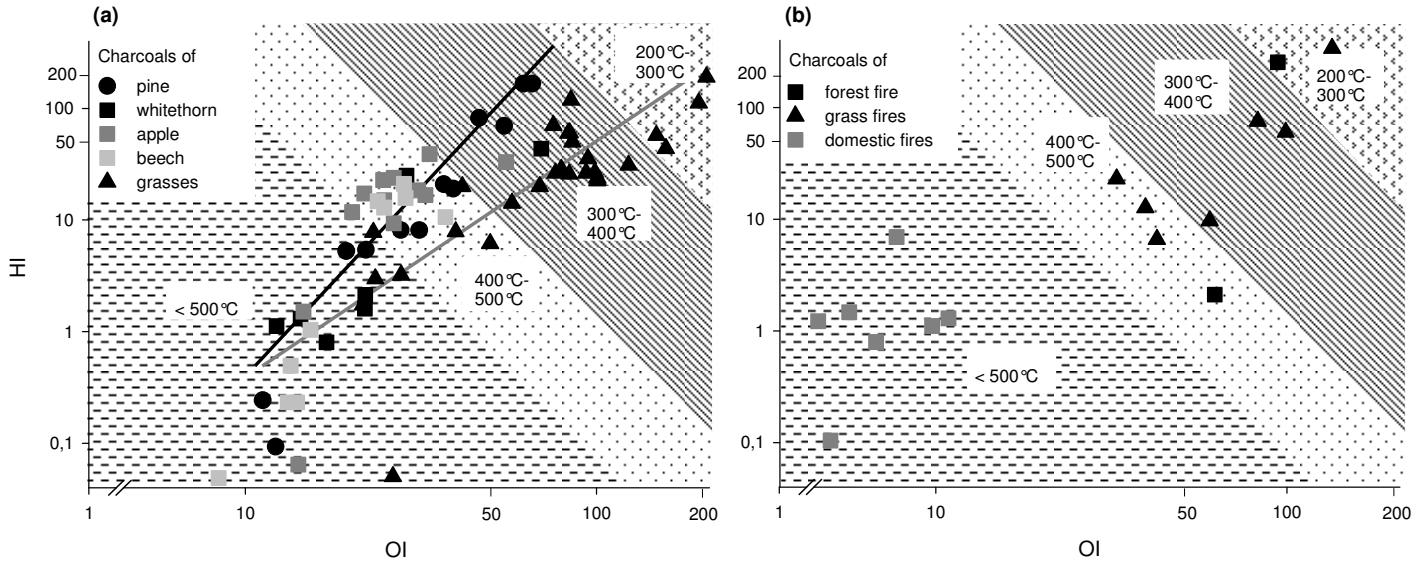


Figure 3

Figure4

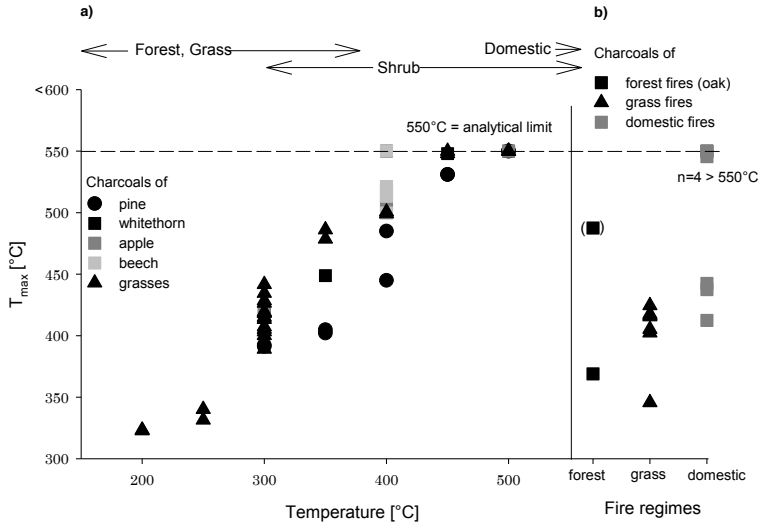


Figure 4

Figure5

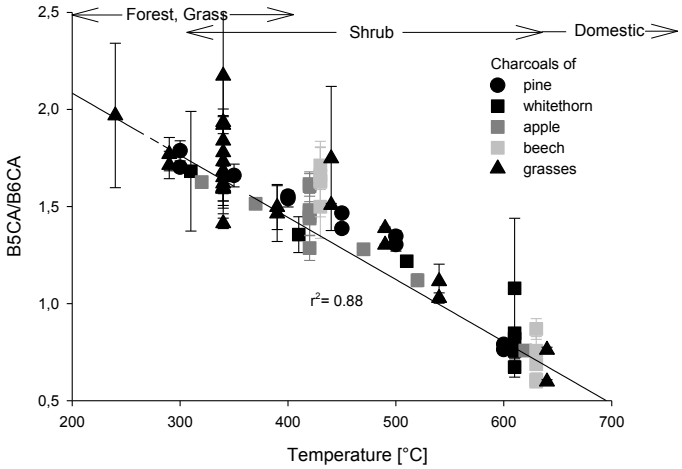


Figure 5

Figure6

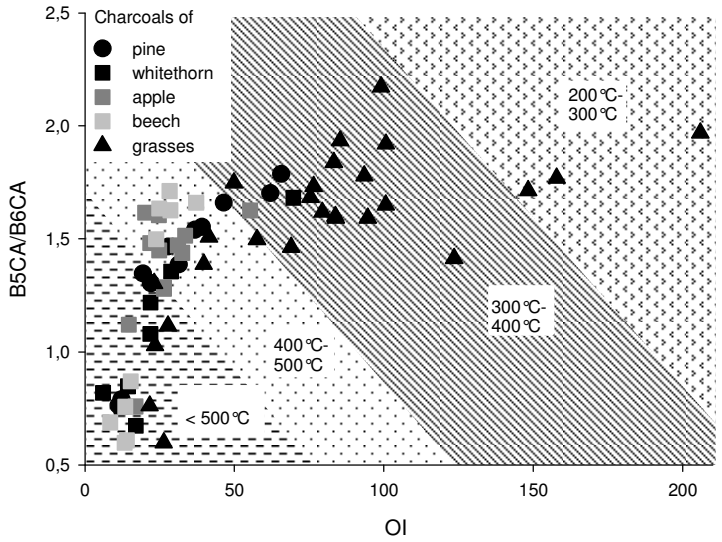


Figure 6

Figure7

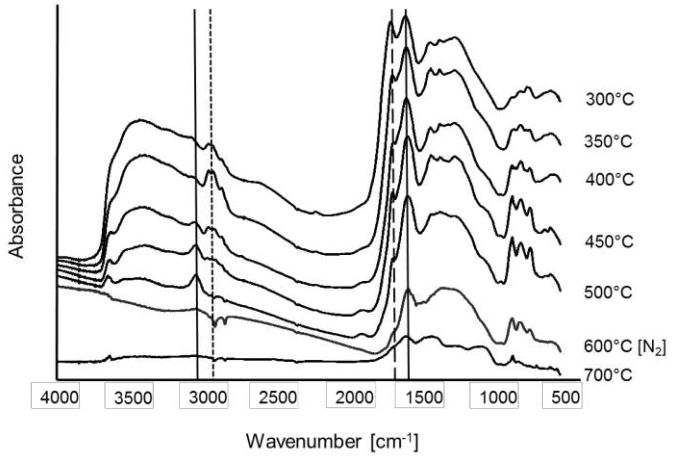


Figure 7

Fig8 revised

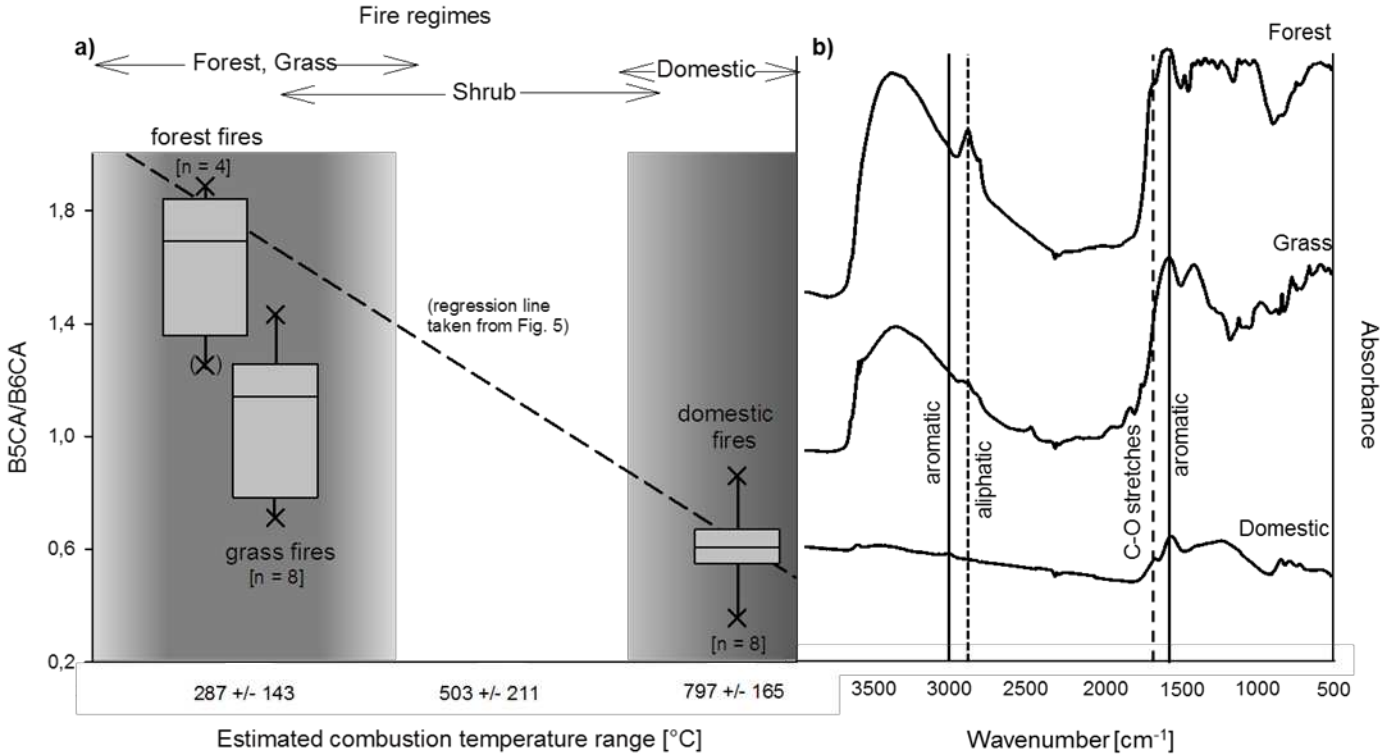


Figure 8

Table 1

Experimental setting	Target temperature (°C)	Heating rate (°C $min^{-1)}$	Heating duration (h)
A	600	10	1; 2; 3; 4; 12
B	300 (grass); 400 (wood)	5	0.5; 1; 2; 3; 4; 12
C	300-700	10	3

Table 2

Vegetation type	Windspeed range [m s^{-1}]	Windspeed median [m s^{-1}]	Temperature range [°C]	Median temperature and SD [°C]	References
forest (n=12)	n.n.	7.6 (n=2)	120 - 621	287 ± 151	Beadle, 1940; Bently and Fenner, 1958; Bailey and Anderson, 1980; Rundel, 1983; Sackett and Haase, 1992; Archibold et al., 1998; Keeley and McGinnis, 2007; Massman et al., 2008; Wanthonghchai et al., 2008
grass and straw (n=30)	2.2 - 16.5 (n=13)	3.1 (n=13)	82.5 - 555	283 ± 134	Sampson, 1944; Miller et al., 1955; Bently and Fenner, 1958; Ito and Iizumi, 1960; McKell et al., 1962; Smith and Sparling, 1966; Stinson and Wright, 1969; Archibold et al, 1998; Busse et al., 2005; Sah et al., 2006; Alexis et al., 2007
shrubland (n=37)	1.5 - 12 (n=29)	6 (n=29)	70 - 1042	503 ± 211	Bently and Fenner, 1958; Whittaker, 1961; Kenworthy, 1963; Countryman, 1964; Stinson and Wright, 1969; Bailey and Anderson, 1980; Hobbs and Grimingham, 1984; Archibold et al, 1998; Neary et al., 1999; Sah et al., 2006; Alexis et al., 2007
domestic fires (n=18)	n.n.	n.n.	317 - 950	797 ± 165	Shepard, 1956; Wells, 1960; Tylecote, 1962; Rowlett et al., 1974; Gibson and Wood, 1997; Martineau and Pétrequin, 2000; Livingstone-Smith, 2001; Fraser et al., 2003; Cohen-Ofri et al., 2006; Braadbaart and Poole, 2008; Maggetti et al., 2011

985 ## Highlights

986 • Combustion residues preserve information of past burning events.
987 • Literature review differentiates three typical fire regimes by
988 temperature.
989 • Geochemical fingerprints for typical fire regimes established from
990 laboratory charcoal.
991 • Fingerprints validated on natural charcoal samples.

992